Thermodynamic Properties of HFC-143a (1,1,1-Trifluoroethane)

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ABSTRACT

An equation of state for HFC-143a has been developed in this study by using the updated information. The present equation of state for HFC-143a is effective both in the superheated gaseous phase and compressed liquid phase at pressures up to 35 MPa, densities to 1327 kg/m³, and temperatures from the 164 K to 433 K, respectively.

Correlations of ideal gas heat capacity, vapor pressure and saturated liquid density are also presented.

Keywords: 1,1,1-trifluoroethane, critical parameter, equation of state, heat capacity, HFC-143a, *PVT* property, saturated liquid density, vapor pressure.

INTRODUCTION

R-502, an azeotrope of HCFC-22 and CFC-115, was widely used in the commercial refrigeration industry for low and medium evaporating temperature systems. Since the concern about the environmental issues is increasing, R-502 was phased out due to it's strong ozone depletion effect and global warming impact. There is no single-component refrigerant to replace R-502, and a binary mixture of HFC-125 and HFC-143a and a ternary mixture of HFC-125, HFC-134a and HFC-143a are considered as the most probable substitutes to replace R-502.

We have reported equations of state for HFC-134a[1], HCFC-123[2], HFC-32[3], HFC-125[4] based on the available thermodynamic property measurements. All these equations of state were developed in a same functional form: the 18-coefficient modified

Benedict-Webb-Rubin equation of state. This 18-coefficient mBWR equation of state was proposed by the present author[1], and was successfully applied to the other refrigerants.

Many experimental studies of the thermodynamic properties of HFC-143a, i.e., *PVT* properties, saturation properties, critical parameters, heat capacities, speed of sound, 2nd virial coefficients, and ideal gas heat capacity, have been reported.

In this study, we applied the 18-coefficient MBWR equation of state to HFC-143a by using the reported reliable information.

EXPERIMENTAL DATA

There are 15 experimental studies[5-19] available reporting more than 450 points of vapor pressure of HFC-143a. On the basis of the selected vapor pressure measurements[9,13-15,17,19], a vapor pressure correlation has been developed.

$$ln(P_r) = 1/T_r [a_1 (1-T_r) + a_2 (1-T_r)^{1.2} + a_3 (1-T_r)^3 + a_4 (1-T_r)^6]$$
 (1)

where $P_{\rm r}=P/P_{\rm c}$, $T_{\rm r}=T/T_{\rm c}$, and the coefficients of Eq.(1) are listed in Table. 1. The critical temperature of $T_{\rm c}=345.88\pm0.01$ K adopted in Eq.(1) was reported by Higashi and Ikeda.[20]. The critical pressure of $P_{\rm c}=3764\pm3$ kPa was then

 Table 1. Coefficients of Eq.(1)

 i
 a_i

 1
 -7.66014815290

 2
 1.42667111715

 3
 -1.79880415911

 4
 -4.48124932092

determined from the above selected vapor pressure measurements[9,13-15,17,19] at the critical temperature of 345.88 K. Equation (1) represents almost all of the selected vapor pressure measurements[9,13-15,17,19] within ±2 kPa. Equation (1) is considered to be effective from 160 K to the critical temperature.

On the other hand, there are 9 studies[5,8,12,17,20-24] for the saturated liquid densities of HFC-143a reported more than 190 saturated liquid densities. Based on the selected measurements[8,17,20-21,23-24], a correlation of the saturated liquid density has been developed as follow:

$$\Gamma_r = 1 + b_1 (1-T_r)^{0.325} + b_2 (1-T_r)^{0.6} + b_3 (1-T_r) + b_4 (1-T_r)^3$$
 (2)

where $r_r = r/r_c$, $T_r = T/T_c$, $T_c = 345.88 \pm 0.01$ K is the critical temperature and $r_c = 431 \pm 3$ kg/m³ is the critical density of HFC-143a reported by Higashi and Ikeda[20]. This correlation is applicable for temperatures from 160 K to the critical temperature.

| Table 2. Coefficients of Eq.(2) | | | | | | |
|---------------------------------|-----------------|--|--|--|--|--|
| i | b_i | | | | | |
| 1 | 1.79883623564 | | | | | |
| 2 | 0.437480200287 | | | | | |
| 3 | 0.576680799911 | | | | | |
| 4 | 0.0604322319815 | | | | | |

Equation (2) represents almost all of the available saturated liquid densities within 0.2 %, expect those in the vicinity to the critical point.

More than 2930 experimental data points *PVT* properties[7,10-11,13-17,19,21,24-25] have been reported. The available experimental data cover a wide range of temperatures from 164 K to 433 K, densities up to 1327 kg/m³, and pressures up to 35 MPa, respectively. Figure 1 shows the distribution of the available *PVT* measurements.

Russell et al.[5] reported 11 points of isobaric heat capacity along saturated liquid line, Magee[17] reported 135 points of isochoric heat capacity, and Nakamura et al.[26] reported 1 point of isochoric heat capacity data in the liquid phase. Haynes[27], and Gillis[28] reported 178 and 171 points of speed of sound data in the vapor phase, Takagi[29] reported 159 points of speed of sound data in liquid phase, respectively.

For the ideal gas heat capacity, there are 7 studies[21,27-28,30-33] reported 60 points of ideal gas heat capacity data. An ideal gas heat capacity correlation has been developed based on these measurements.

$$C_p^0/R = c_1 + c_2_T_r + c_3_T_r^2 + c_4_T_r^3$$
(3)

where $T_r = T/T_c$, the coefficients of Eq.(3) are listed in Table 3. As shown in Fig. 2, the correlation of ideal gas heat capacity represents almost all of the measurements within 1.5 %.

| Table 3. Coefficients of Eq.(3) | | | | | |
|---------------------------------|----------------|--|--|--|--|
| i | c_{i} | | | | |
| 1 | 1.42541931841 | | | | |
| 2 | 11.5570619103 | | | | |
| 3 | -2.92707403102 | | | | |
| 4 | 0.279478085285 | | | | |

MODIFIED BWR EQUATION OF STATE

We have proposed an 18-coefficient MBWR equation of state for HFC-134a[1] in 1993. This equation has been applied to several other refrigerants, i.e. HFC-32, HFC-

125, and HCFC-123, successfully. In this study, we apply our equation of state to HFC-143a by using the updated measurements. The input data of the least square fitting procedures include *PVT* data, saturation data, Maxwell's equal area construct, thermodynamic restrictions at the critical point, isochoric heat capacities, and speed of sound data. The saturation data, i.e., the vapor pressures coupled with the saturated vapor/liquid densities, and the Maxwell's equal area construct, i.e., the thermodynamic restriction of Gibbs free energy of the saturated vapor and the saturated liquid being equal at the same temperatures, were calculated from Eq.(1), Eq.(2), and a supplementary correlation of saturated vapor density developed in the present study, since it is difficult to get the pairs of the vapor pressure data and the saturated vapor/liquid data measured exactly at the same temperatures. The thermodynamic constraints which at the critical point include the conditions that pressure being exactly consistent with the critical pressure and the first and the second density differentials of pressure to be zero at the critical point, respectively. The ideal gas heat capacity was calculated from Eq.(3).

The 18-coefficient MBWR equation of state has finally been developed as follows:

$$P_{\rm r} = T_{\rm r} r_{\rm r}/Z_{\rm c} + B_{\rm 1} r_{\rm r}^{2} + B_{\rm 2} r_{\rm r}^{3} + B_{\rm 3} r_{\rm r}^{4} + B_{\rm 4} r_{\rm r}^{5}$$

$$+ B_{\rm 5} r_{\rm r}^{6} + B_{\rm 6} r_{\rm r}^{7} + (B_{\rm 7} + B_{\rm 8} r_{\rm r}^{2}) r_{\rm r}^{3} \exp(-r_{\rm r}^{2})$$

$$(4)$$

where $P_r = P/P_c$, $r_r = r/r_c$, $T_r = T/T_c$, $Z_c = P_c / (R_x r_c r_c)$, $R_x = R/m$; $P_c = 3764$ kPa, $r_c = 431 \text{ kg/m}^3$, $T_c = 345.88$ K, R = 8.314471 kJ/(kmol K), m = 84.041 kg/kmol.

$$\begin{split} B_1 &= d_1 T_r + d_2 + d_3 / T_r^2 + d_4 / T_r^3 \\ B_2 &= d_5 T_r + d_6 + d_7 / T_r^2 \\ B_3 &= d_8 + d_9 / T_r^2 \\ B_4 &= d_{10} + d_{11} / T_r \end{split} \qquad \begin{split} B_5 &= d_{12} + d_{13} / T_r \\ B_6 &= d_{14} \\ B_7 &= d_{15} + d_{16} / T_r \\ B_8 &= d_{17} + d_{18} / T_r \end{split}$$

All of the thermodynamic properties can be calcualted from Eq.(3) and Eq.(4) with the aid of the general thermodynamic equations.

DISCUSSION

Figure 3 shows the comparison of the measured *PVT* property data and the present equation of state, Eq. (4), in the pressure deviation for the superheated gaseous phase and the supercritical region(0<r<600 kg/m³), and Fig. 4 shows the comparison in the compressed liquid phase(r>600 kg/m³), respectively. The detailed results are listed in Table 4.

Table 4. Summary of the comparison of the *PVT* data and Eq. (4)

| Author | Year | Ref. | dP/P [%], (0 <r <600="" kg="" m<sup="">3)</r> | | $dr/r [\%], (r>600 kg/m^3)$ | |
|-----------|--------|-------|---|-----------|-----------------------------|-----------|
| | | No. | | | _ | |
| | | | Std. Dev. | Max. Dev. | Std. Dev. | Max. Dev. |
| Mears | 1955 | 21 | 1.5 | 2.7 | | |
| Takahashi | 1990 | 7 | 0.73 | 5.7 | | |
| Ye | 1993 | 10 | 0.26 | -1.4 | | |
| Giuliani | 1994,5 | 11,15 | 0.17 | -0.51 | | |
| de Vries | 1995 | 13 | 0.17 | 1.6 | 0.25 | -3.1 |
| Fujiwara | 1995 | 14 | 0.47 | 1.0 | | |
| Zhang | 1995 | 16 | 0.10 | -0.46 | | |
| Defibaugh | 1996 | 24 | 1.2 | -2.3 | 0.19 | 0.99 |
| Magee | 1996 | 19 | | | 0.074 | -0.25 |
| Weber | 1996 | 19 | 0.15 | -0.47 | | |
| Nakamura | 1997 | 25 | 0.60 | 1.8 | 0.23 | -0.67 |

Figure 5 is the comparison of measured vapor pressures with Eq. (4). The Eq. (4) represents almost all of the selected vapor pressure measurements[9,13-15,17,19] within ± 2 kPa. The deviations of measurements by Magee[17] at the temperature below 200 K increase up -2.5 %, but the absolute deviations are less than ± 0.044 kPa.

Figure 6 shows the comparison of saturated liquid densities with Eq. (4). The selected saturated liquid densities [8,17,20-21,23-24] show a good agreement with the equation of state, within ± 0.2 %, except the measurements are very close to the critical point.

The present equation of state also represents the C_P and C_V data reported in liquid phase by Russell et al.[5] with a maximum deviation of -0.61 % and a standard deviation of 0.37 %, and Magee[17] with a maximum deviation of 6.7 % and a standard deviation of 1.4 %, as shown in Fig. 7. The measurement reported by Nakamura[26] was also represented with a deviation of -1.0 %. Figure 8 shows the comparison of the speed of sound data with the equation of state, Eq. (4). The speed of sound measurements reported in superheated gaseous phase by Haynes[27] and Gillis[28] are represented with

maximum deviations of 0.23 % and -0.14, standard deviations of 0.048 % and 0.045, respectively. The speed of sound in liquid phase by Takagi[29] were presented with a maximum deviation of 2.0 %, and a standard deviation of 0.93 %.

Figure 9 compares the behavior of the temperature dependence of second virial coefficients calculated from the present equation of state with the reported data by, Ye[10], Zhang et al.[16], Gillis[28], Beckermann and Kohler[33], and Bignell and Dunlop[34]. These results show a good agreement with each other.

CONCLUSION

A vapor pressure correlation, a saturated liquid density correlation, and a ideal gas heat capacity correlation have been developed for HFC-143a, based on the available measurements.

An 18-coefficient MBWR equation of state for HFC-143a has been developed. This equation of state is considered to be effective in the range of temperatures from 160 K to 433 K, densities up to 1430 kg/m³ and pressures up to 35 MPa.

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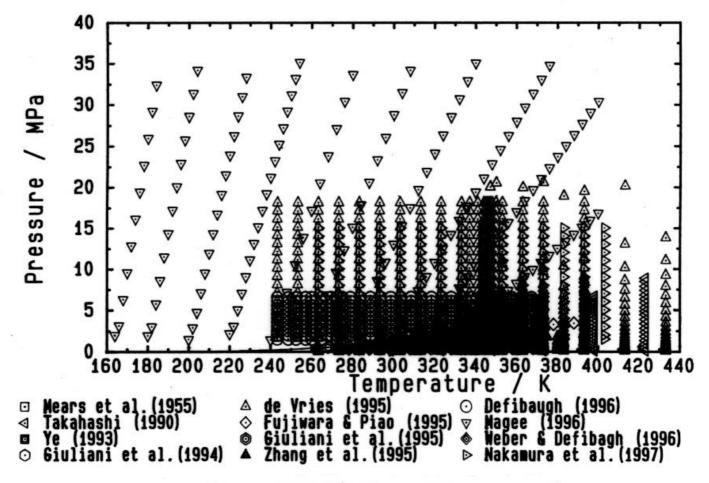


Figure 1 Distribution of the PVT measurements

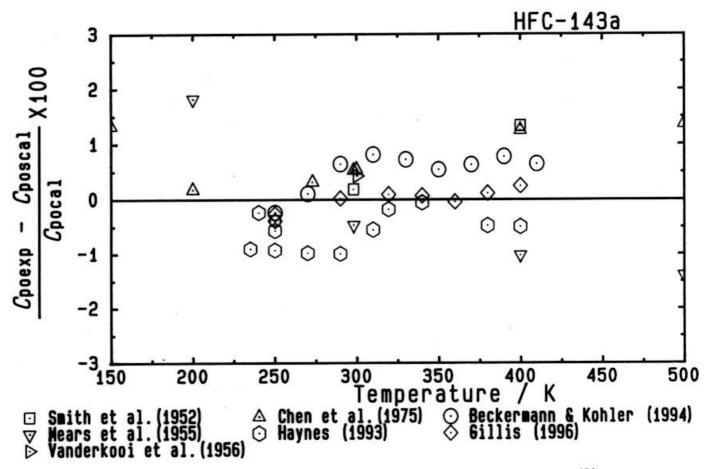


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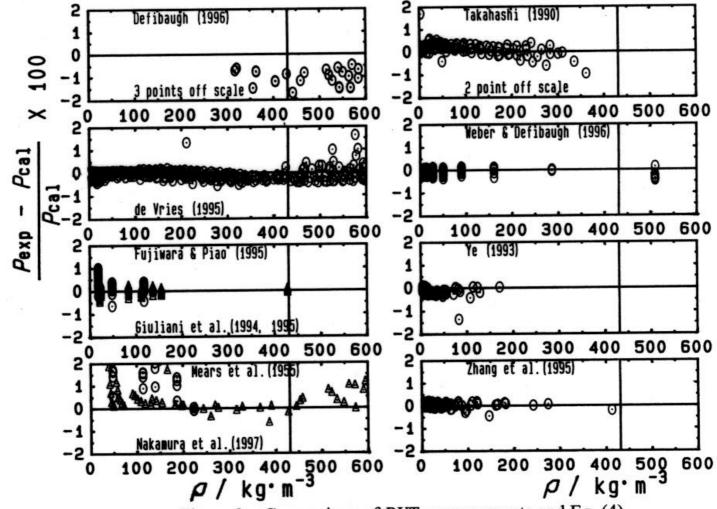


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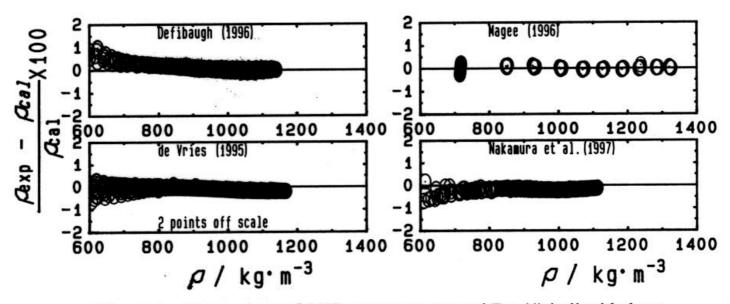


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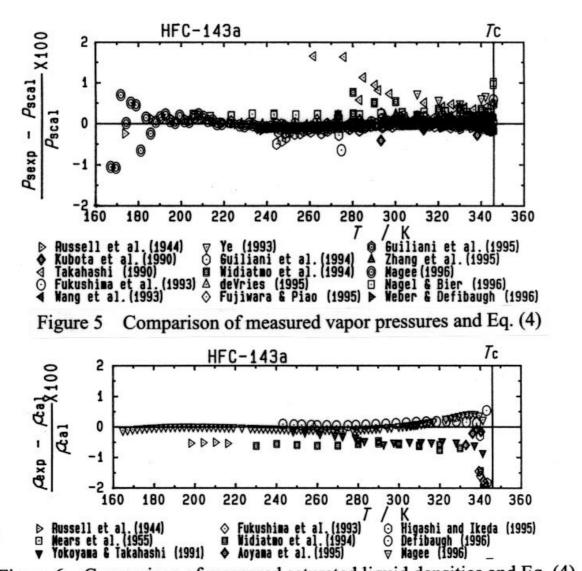
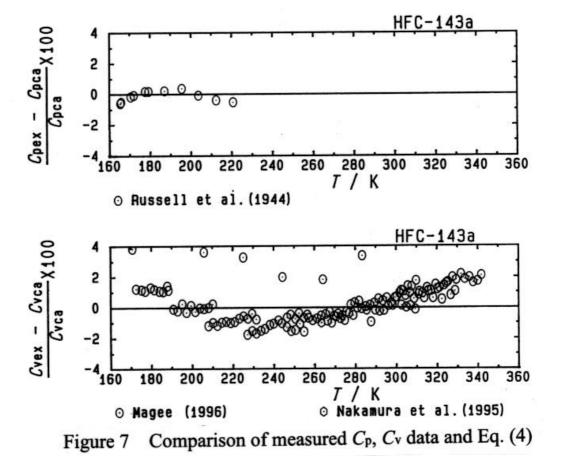


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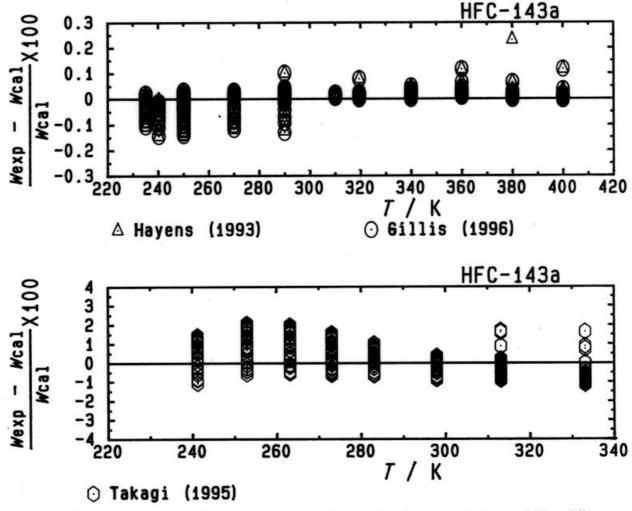


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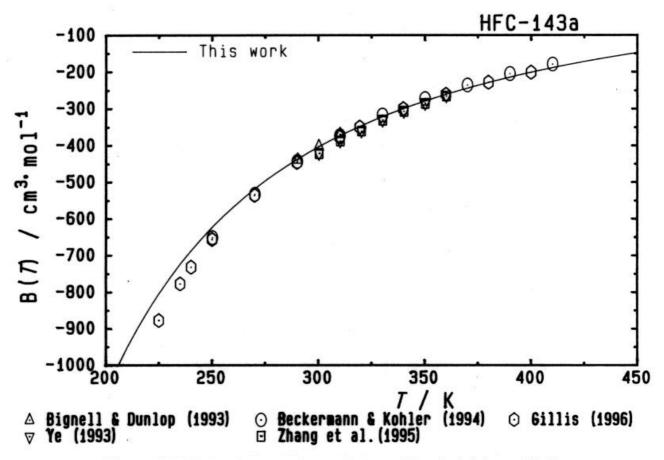


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